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THE PROGRESS IN THE STUDY OF SEMICONDUCTOR MATERIALS,(U)
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THE PROGRESS IN THE STUDY OF
SEMICONDUCTOR MATERIALS

by

Hsu Chen-Chia

FOREIGN TECHNOLOGY DIVISION

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THE PROGRESS IN THE STUDY OF SEMICONDUCTOR MATERIALS

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The Progress in the Study of Semiconductor Materials (2)

Hsu Chen-chia

3. Other Semiconductor Materials

There are some other areas from which semiconductor materials can be found and to which the materails can be applied. They are solid solutions of Group 111-V and Group 11-VI compounds; heterogeneous junction of chemical compounds; various ternary and higher compounds; and amorphous semiconductor.

By the rules concluded in crystal chemistry, and according to the tendency of periodic table change, a great amount of semiconductor ternary and higher compounds can be made, such as $A^{I}B^{III}C^{VI}$, $A^{II}B^{IV}C_2^{V}$ ... . Among these compounds, $ZnSiP_2$, $CdGaAs_2$ have arrested people's attention because they show characteristics which bear resemblance to those of Group 111-V compounds. On the other hand, by combining binary compounds which have become well known, it can produce numerous semiconductor polynary compounds, such as (111-V)-(11-V1), (111-V)-(11 1V V_2), (111-V)-(1 111 V_2). This kind of work was very active in the middle 1950's, but, except for some theoretical exploration, the prospect of application is not clear. Here is no attempt to make any further discussion.

1. $GaAs_{1-x}P_x$ is a solid solution which has developed very rapidly in recent years. As indicated in Table 5, this material can be used to make solid digit display tube. Because of the use for model display in computers, the production of this light-emitting article by some countries is annually more than 4×10^7 pieces. $GaAs_{1-x}P_x$ is prepared mainly by using vapor

phase epitaxy method, such as using $Ga/AsH_3/PH_3/HCl/H_2$ or $Ga/AsCl_3$ (or PCl_3)$/As_3H_3$ (or pH_3)$/H_2$ and GaAs as substrate. It is easy using this method to regulate the components and thereby to have various kinds of light length. It is good for bulk production. After being mixed with N_2, the material can produce 5890Å yellow light. There is also a lot of $Ga_{1-x}Al_xAs$. To prepare this material is to use liguid phase epitaxy method, when $x = 0.38$, it can produce 6,600Å red light.

In recent years, quite few people work on such solid solutions as $In_xGa_{1-x}As$, $InAs_xP_{1-x}$, $In_xGa_{1-x}As_yP_{1-y}$ mainly because these materials can be used to make negative electronic affinity photoelectric anode. Of such anode, the photoelectricity is highly sensitive, and dark current is small. After the component of this solid solution is regulated, it can be used to design spectral characteristics. But there is still a number of problems to be solved, such as how to use this material to make photoelectric anode penetration pattern; how to make curve focusing plane which the photoelectric anode is used to use; how to get a large scale material of several tens of square cm; and how to continuously cover the CsO layer ~~wihtout~~ without having to break away from vacuum. So the anode of this kind is still at the stage of being studied and its future development is quite promising.

Of Group 11-V1 compound solid solution that which has been studies the most is $TeCd_xHg_{1-x}$. It is very useful infrared probe material, and it can be used to make eigen probe of 8-14 micron (atmosphere transparent window). Currently the study mainly covers crystal of $0.15 < x < 0.40$. In addition, $ZnSe_xTe_{1-x}$ $(0.6 \geq x \geq 0.1)$, $Zn_xCd_{1-x}Te$ $(x \leq 0.4)$, $Mg_xCd_{1-x}Te$ $(x \leq 0.4)$ have

also been studied. They are also materials used to make infrared probes.

2. The boundary where two different kinds of semiconductors are bended together is called heterogeneous junction. If the two semiconductors are both n type (or p type), the boundary is called isotype ~~iostype~~ heterogeneous junction. If the types of electric conduction of two semiconductors are opposite to each other, the boundary is called opposing type heterogeneous junction. Such ideas were advanced twenty years ago, and because of their recent gaining in practical application, they have caught great attention. A single heterogeneous junction ($nGaAs-PGaAs-PGa_{1-x}Al_xAs$) laser can make the density of threshold current at room temperature several degrees lower than homegeneous junction, and double heterogeneous junction ($nGa_{1-x}Al_xAs-PGaAs-PGa_{1-x}Al_xAs$) lasers at room temperature continuously interfer each other. Now the scope of study on heterogeneous junction has greatlly been expanded.

The main condition under which the heterogeneous junction can grow well is the match of crystal lattice. Table 6 gives the data of the commonly well known materials. When the crystal lattice of two sets of materials does not match, a polyboundary plane will be formed at the boundary, and the property of heterogeneous junction will therefore become low. The crystal lattice constant difference of GaAs and Ge is 0.5%, and it is a heterogeneous junction which has been successfully studied. The crystal lattice constant difference of GaAs and AlAs is 0.14%, so the heterogeneous jnuction of $Ga_{1-x}Al_xAs-GaAs$ is also a successful one. For solid solution, by regulating the components, it can make the crystal lattice constant unmatchedness the minimum. For instance, the crystal lattice constant unmatchedness of GaAs-GaP

is 3.6%, but in $GaAs_{0.6}P_{0.4}$, it can be regulated into 1.4%. This is the material used in light-emitting diode. The heterogeneous junction materials which are widely under study at the present time include: $GaAs-GaAs_{1-x}P_x$, $GaP-Ga_{1-x}Al_xAs$, Ge-Si, GaP-Si, ZnSe-ZnTe, GaAs-ZnSe, (or InSe), $InAs_{1-x}P_x-InAs$ (or InP), $Ga_{1-x}In_xAs-GaAs$, $GaP-In_xGa_{1-x}P$. The contents of these studies are mainly the semiconductor fundamental physical phenonmena, which can be classified into two aspects: transport process and photoelectric nature. Of transport process, it studies the characteristics of volt-ampere under the pressure of positive and reverse voltage, and discovers that the electric currents are of two parts: one is affected by temperature and the other is not. Of the photoelectric nature, it explores the photoelectric process of isotype as well as opposing type hetergeneous junction, and the impact of boundary

Table 6 Data of Crystal Lattice Match of Materils

Metal Series		Cryst. lattice Constant A		Crystal lattice Const. diff.	Melting point (°C)		Forbidden band width (eV) 300°K	
A	B	A	B	Δa, %	A	B	A	B
Ge	GaAs	5.6575	5.653	0.5	937	1238	0.663	1.43
Si	GaP	5.4307	5.451	2	1415	1465	1,120	2.26
AlP	GaP	5.451	5.451	<0.01	2550	1465	2.4	2.26
AlSb	AlP	6.135	5.451	11.8	1050	2550	1.65	2.4
AlSb	AlAs	6.135	5.661	8	1050	1740	1.65	2,16
AlP	AlAs	5.451	5.661	3.8	2550	1740	2.4	2.16
AlAs	GaAs	5.661	5.653	0.14	1740	1238	2.16	1.43
AlAs	InAs	5.661	6.057	6.7	1740	937	2.16	0.35
AlSb	InSb	6.135	6.479	4.7	1050	530	1.65	0.17
AlP	InP	5.451	6.057	10.5	2550	1070	2.4[illegible]	0,34
InSb	GaSb	6.479	6.095	6.1	530	712	0.17	0.73
InAs	GaAs	6.058	5.653	6.9	937	1238	0.35	1.43
InP	GaP	5.869	5.451	7,3	1070	1465	1.34	2,26
InAs	InP	6.057	5.870	3.2	937	1070	0.36	1.34
InAs	InSb	6.057	6,479	6.8	937	530	0.35	0.17
InSb	InP	6.479	5.869	10	530	1070	0.17	1.34
GaAs	GaP	5.653	5.451	3.6	1238	1465	1.43	2.26
GaAs	ZnSe	5.653	5.6687	1.5	1238	1515	1.43	2.6
GaSb	AlSb	6.095	6.135	0.65	712	1050	0.73	1.65
GaSb	GaAs	6.095	5,653	7.5	712	1238	0.73	1.43
GaSb	GaP	6.095	5.451	11.1	712	1465	0.73	2.26

plane on the photoelectric effect. But because of the lack of understanding of boundary plane, the study in this respect is till at the beginning stage, and the prospect of application is not clear.

Because of the consideration of the techniques in integrated circuit and optical integration, recently there have been quite few studies on the subject of compound epitaxy on insulated substrate. The general situation is indicated in Table 7.

Table 7 The General Situation of Compound Semiconductor Heterogeneous Epitaxy

Compound	Substrate	Technique	Growth rate (Å/)	Epi-temp. (℃)	Parallel cryst. dir. deposit/substrate
GaAs	Al_2O_3	chemical vapor phase deposit	~1100	~700	(111)/(0100), (1$\bar{1}$0)/(1120)
	$MgAl_2O_4$	chenical vapor phase deposit	—	700	(100)/(110)
	CaF_2	molecule beam epitaxy	—	~540	--/(111)
	BeO	thermal decomposition	—	—	—
	ThO_2	thermal decomposition	—	—	—
	$MgGa_2O_4$	liquid phase epitaxy	—	—	—
GaP	Al_2O_3	chemical vapor phase deposit	8000	800	(111)/(0001)
	$MgAl_2O_4$	chemical vapor phse deposit	8000	700	(111)/(111)
	Si	liquid epitaxy thermal decomp.	5000	—	—
GaN	Al_2O_3	CVD thermal decomp.	—	925	(0001)/(0001)
	Si	thermal decomposition	—	—	—
InAs, InP	Al_2O_3	chemical vapor phase deposit	~500	700--725	(111)/(0001)
$Ga_{1-x}In_xAs$	Al_2O_3	chemical vapor phase deposit	~1000	~700—755	(111)/(0001)
$GaAs_{1-x}P_x$ ($x = 0.1 - 0.6$)	Al_2O_3	CVD(triply primitive Ga-AsH_3-PH_3)	—	700--725	
$GaAs_{1-x}Sb_x$ ($x = 0.1 - 0.3$)	Al_2O_3	CVD(triply primitive Ga-AsH_3-SbH_3)	—	725	

3. There are areas in the study of semiconductor materials, which caught great attention in the very beginning. They are the so-called magnetic semiconductor, superconductive semiconductor and rare earth semiconductor. In the early 1950's, someone thought that magnetic semiconductor was non-existent. But from the study of europium sulphide, it has been found that this kind of ferromagnetic material clearly has the characteristics of semiconductor. The materials include: EuO, EuS, $EuSe$; MnP; VO_2; $GeTe$–$MnTe$; $CdCr_2S_4$, $ZnCr_2S_4$. In one material, there exist two basic physical features--magnetism and semiconduction, it is rather significant in theory as well as in application. Same is the case of superconductive semiconductor, such as $SrTiO_3$, $Ge_{1-x}Te$ $(x > 0)$.

There is another special semiconductor that is amorphous semiconductor. The amorphous semiconductor materials, which have so far been known, are of two major groups: sulphide amorphous semiconductor and oxide semiconductor. Sulphide series are selected from among those elements of Ge, Si, As, Te, Se, and S, and by different ratio they are made into binary, ternary and higher compounds, such as As-S, As-Se series and As-Te-Ge series. The oxide series are by different ratio made from B_2O_3, BaO, V_2O or B_2O, CaO, Cu_2O. The main characteristic of amorphous semiconductor is that the atoms (molecule, ion) will make no more periodic and regular arrangement, and its good points are that the techniques required for preparing it are simple; the effect of the minute amount impurity is not great; the integrity of articles made of it is high; working cost is low; and ability of radiation resistance is strong. The areas which have so far been explored for application are switch and memory device. Of a switch, the switching time is short but the

duration of relaxation is very long. The structural problem (heat or elecricity) is not clear, so the prospect of application is not promising. Applied to memory device, such as main read memory, the problems of stability, reliability and repeatability have not yet been satisfactorily solved. Others like photographic target, "latent image" and photocrystal used in holograph are all under study. In short, for making practical application of amorphous semiconductor possible, a lot of work in the area of theory, phenomena analysis and technology has to be done.

4. Technology in Preparing of Semiconductor Materials

The technology used in preparing semiconductor materials has been neglected for it is sometimes mistaken as a kind of simple technique. In fact, however, technology is an important area in the study of semiconductor materials.

1. Nowadays, a large or a medium integrated circuit in a factory is often carrying on programs of production to produce by a rate of several million pieces per month. So to produce silcon epi-sheet in great quantity has become an important task. It includes isodiameter single crystal growth; production of silcon sheets; thickness of the epi-sheets in large quantity; strict control of concentration and distribution of impurity; and the guarantee of the epi-sheet crystal perfection. It requires numerous technological studies in order to solve these problems. So far it has been possible to have silcon single crystal (isodiameter control, equal standing, [111] or [100]) of 90% sold as silcon sheets. A uniform cutting , grinding and selecting suitable physical parameter can therefore save manpower and cost and can also promote quality and quantity. Of the epi-sheet of 10 micron,

the thickness fluctuation can be controlled by 5%, but for the epi-sheet of 2-3 micron, it is still difficult to control to the same degree. In order to control thickness fluctuation, it must strictly control the fluctuation of growth temperature and the responsiveness to the concentration of silconide (such as $SiCl_4$, SiH_4) in the air. For achieving impurity evenness, it must control the relationship between the state of air flow and impurity concentration.

As everyone knows that the perfection of material will greatly affect the property of an article made of that material. In the past, however, attention was largely given to the study of material perfection and overlooked the defects caused by high temperature oxidation and latent diffusion in the technological process of an article. That is the so-called secondary defect. Now, the perfect crystal article technology is that which combines material technology and article technology, and emphasizes on overcoming secondary defect. The technique of grinding and polishing silcon sheets, for example, uses temperature method to form smooth epi-layer with definite thickness and uses double adaptation method to avoid lattice distortion caused by too much or too little impurity. All these techniques are good for promoting property (such as lowering noise) and quality of articles.

2. As a result of the development of semiconductor article technology, now it generally requires a thin layer formed on the substrate. Silcon epitaxy is a well known example. In fact, a thin layer as required by technology can be a semiconductor, an insulator or a metal, and this thin layer can serve as inductor and sometime as an insulator or both. Because of the importance of such a thin layer in technological process, a technique

is therefore hoped to be of good repeatability, short processing time and low cost so that it can be used to produce thin layer with definite chemical as well as physical characteristics. The chemical vapor phase deposit method (CVD) is the technique which has developed rapidly and received great attention. The situation of its application to semiconductor can be seen in Table 8. The chemical vapor phase deposit method is to use vapor compound or mixture acting on a heated surface to form the thin layer as required. This method is simpler than vocuum vaporization or splashing, and it takes less time and sometimes its temperature can be lowered. As indicated in

Table 8 Application of Chemical Vapor Phase Deposit to Semiconductor Technology

	Kind of film	Formation Method	Application
Silcon	Si single crystal	$SiCl_4 + H_2 \xrightarrow{1200℃} Si + HCl$ $SiH_2Cl_2 + H_2 \xrightarrow{1150℃} Si + HCl$ $SiH_4 \xrightarrow{1100℃} Si + H_2$	Plane crystal tube Double-electrode integrated circuit
Silcon	Si poly-crystal	$SiH_4 \xrightarrow{700-900℃} Si + H_2$	Silcon grid of MOS integrated circuit
Insulated Film	SiO_2	$SiH_4 + O_2 \xrightarrow{300-500℃} SiO_2 + H_2$ $SiH_4 + CO_2 + H_2 \xrightarrow{800-950℃} SiO_2 + CO + H_2O$ $Si(OC_2H_5)_4 \xrightarrow{700-800℃} SiO_2 + C_2H_4 + H_2O$	Al composite line protection film. surface protection film, multi-layer composite line insulating film Oxidized film corrosion cover Oxidized film corrosion cover
Insulated Film	Phosphor silicate glass (PSG) Boro-silcate glass (BSG)	$SiH_4 + PH_3 + O_2 \xrightarrow{350-500℃} SiO_2 + P_2O_5 + H_2O$ $SiH_4 + B_2H_6 + O_2 \xrightarrow{350-500℃} SiO_2 + B_2O_3 + H_2O$	Surface protection film, diffusing source
Insulated Film	Si_3N_4	$SiH_4 + NH_3 \xrightarrow{800-950℃} Si_3N_4 + H_2$ $SiCl_4 + NH_3 \xrightarrow{1000℃} Si_3N_4 + HCl$	Surface protection film (MOS, DHD, beam lead) Oxidation diffusion covering film (isoplanar isolator)
Insulated Film	Al_2O_3	$AlCl_3 + CO_2 + H_2 \xrightarrow{850-950℃} Al_2O_3 + HCl + CO$ $Al(OC_3H_7)_3 \xrightarrow{400-800℃} Al_2O_3 + C_3H_6 + H_2O$	Surface protection film of MOS integrated circuit Isolating film of multi-layer composed line
Insulated Film	Others	$Ta(OC_2H_5)_5 + O_2 \xrightarrow{600-800℃} Ta_2O_5 + C_2H_4 + H_2O$ $Ti(OC_2H_5)_4 + O_2 \xrightarrow{600-800℃} TiO_2 + C_2H_4 + H_2O$	Surface protection film
Metal	Mo W	$MoCl_5 + H_2 \xrightarrow{600-700℃} Mo + HCl$ $WF_6 + H_2 \xrightarrow{700℃} W + HF$	MOS metal grid, multi-layer composed line Schouky diode

Table 8, this method has been used to produce polycrystal silcon and single crystal silcon, Mo, W, Pt, Si_3N_4, BN, SiO_2, Al_2O_3 . In integrated circuit techniques, such as buried layer, (p-n) junction isolation, collecting electrode, emitting electrode and base electrode, are all completed through impurity diffusion. Solid-solid diffusion is to use chemical vapor phase deposit method first to deposit the impurity source (AsH_3, PH_3, B_2H_6) and then to diffuse them. As the deposition temperature is low, it is easier to control the surface concentration and the junction depth, and the eveness and repeatability are all good, too. The chemical vapor phase deposit method can also be applied to many other areas, so recently the study of this method spreads very rapidly.

3. The quality and quantity of compound semiconductor are far less satisfactory than those of element semiconductor. The main reason for this fact is that there still are many problems existing in the techniques used for preparing semiconductor materials. In Table 9, there is a list of some strong points and shortcomings of the methods used in preparing semiconductor materials. The main difference between compound semiconductor and element semiconductor is that the former has two or more components, so, in addition to the degree of purity, there is a problem of chemcial distribution and proportion. It still has difficulty to measure accurately the chemical proportion, except through some indirect study. In the case of gallium arsenide, for example, through a study of various physical characteristics of arsenic, some of its features are found. At high melting point ($>$1,200°C) and under great dissociation pressure ($>$10 air pressure), the problem becomes even more serious. Taking GaP for example, in a single GaP, the vacancy concentration of Ga or P is estimated above $10^{18}cm^{-3}$. Next is

the staining problem of the reaction system (including container and material container) and compounds action. In the methods used for preparing GaAs, there is a serious Si staining problem. The stain is the result of reaction of Ga (or H_2) against quartz. In GaAs vapor phase epitaxy, someone tries to use $Ga/AsCl_3/N_2$ series and it is hopeful to avoid Si stain. In short, only some inventive work can bring a break through in this field.

Table 9 The Principal Methods of Preparing Compound Semiconductor

Methods	Strong Points	Shortcomings
Grow out of non-chemical apportioned solution	technique equipment is simple (low temperature low pressure) good crystal perfection	small crystal, crystalization rate low, long processing time, low production
Crucible-free zone melting	the stain on the material container is avoidable	Complicated equipment, small diameter single crystal, difficult to use at high temperature ($>1300°C$) and under high pressure (>2 atm.pressure)
Horizontal zone melting (or directional crystalization)	simple equipment, possible to have large single crystal	staining material container, difficult to use at high temperature($>1300°C$) and under high pressure(>2 atm.pressure),long processing time,hard to have crystal perfection
Pulled single crystal	possible to have large single crystal, high crystalization rate,can be used at high temperature, can grow under high pressure, short processing time	complicated equipment,staining material container, poor crystal perfection
Liquidus epitaxy	good crystal perfection, high purity	long processing time,low production, strict requirements in technique, difficult to make good surface and even film. Some compounds cannot use this method
Vapor phase epitaxy (thermal decomposition, disproportionating reaction)	simple technique, high purity, high production	difficult to control technique condition, problems in perfection, homogeneity and repeatability

5. The Characteristic Parameter Test and Analysis of Semiconductor Materials

The characteristic parameter test and analysis of semiconductor material is an important aspect in the study of semiconductor materials. These parameters include data relating crystal structure, components, defects, and physical as well as chemical characteristics of the material to articles made of these materials.

As a result of the development of the semiconductor article, the study of the characteristics of the materials has changed greatly. The general tendency is that the study of semiconductor materials has changed into the study of thin layer and surface; the study of even components and electricity parameter develops into the study of uneven distribution of impurity and various physical characteristics in the microregion; and the study of element semiconductor develops into the study of compound semiconductor, which includes chemical apportionment problems. In order to promote accuracy and to save manpower and time, the whole field of testing has changed to use electronic computer, various automatic instruments and digit display equipment. The parameter test for general use will not be discussed here except for a few points which have been considered important.

1. The articles used widely now are mostly made of epitaxial or other thin layer materials, of which the thickness ranges about 10^{-1}-10^{2} micron. There are single layer and multi-layer, and heterogeneous and homogeneous structures, but their quantity is not large. Taking Si for example, one square cm thin layer of 10 micron weighs only about 2.3×10^{-3} grams. It is very much different to examine impurity and its distribution in a thin layer from examining semiconductor materials. For solving such problems, there

Table 10 Some Thin Layer and Surface Microregion Analysis Methods

(1)

	Ion beam Low energy (0.5-50 KeV)		
Ion beam or electron beam			
Product after acting on samples	scattering ion	splashing ion	photon produced from ion and atom
Names of analysis techniques	back scattering low energy (1-2 KeV)	Ion probe	photon produced from ion
Minimum probe diameter	$\simeq$ 1mm.	(2-70)micron	$\simeq$ 1mm.
Transvers recognition rate	$\simeq$ 1/2mm.	$\simeq$ 1micron	$\simeq$ 1/2mm.
Depth recognition rate (% of total depth)	30%	best 5-10%	best 5-10%
Sampling depth	(1-2)atom layer	(1-5)atom layer	(1-5)atom layer
Consumption of each sample	(1-4)atom layer	$>\frac{1}{4}$ atom layer	$>\frac{1}{2}$ atom layer
Destructive or not	yes	yes	yes
Analysized element	z $\geqslant$ 4	all elements except He, Ne	all elements
Testing limit	0.1 at%	$(0.1-10^3)$ppb, $(10^{-4}-0.1)$at%	-
Accuracy	-	10%	-
Sample necessary or not	necessary	necessary	necessary
Accelerator necessary or not	not	not	not
Remarks			

have been some useful methods developed. The major ones are shown in Table 10.

Ion probe technique is to use ion source bambardment combining with quality tester. It first uses ion beam emitting sample of 1-25 KeV and the sample is splashed. Most of the materials in the form of neutral atom or

Table 10 Some Thin Layer and Surface Microregion Analysis Methods

(2) continued

Electron beam (2 - 10 KeV)		Ion beam (0.1 - 3 MeV)		
secondary electron	X ray	scattering ion secondary electron	X ray	reactant (P, α, γ)
Auger electron spectrum	electron probe	back scattering	X ray produced from ion beam	nucleus reaction
(10-100)micron	(0.2-1)micron	$\simeq$1mm.	$\simeq$1mm.	$\simeq$1mm.
(20-50)micron	(1-2)micron	$\simeq$1/2mm.	$\simeq$1/2mm.	$\simeq$1/2mm.
best 5-10%	limited	$\simeq$200Å	limited	$\simeq$1000Å
(1-5)atom layer	100Å-3micron	(1-3)micron	100Å-3micron	(1-5)micron
negligible	indigestion	negligible	negligible if no ion bombardment	negligible
not	not	not	not	not
$Z > 2$	$Z \geq 4$	active to double element	$Z > 5$	active to light element
$3\times10^{-3}-10^{-1}$ atom layer 0.1 at %	$10^{2}-10^{3}$ppm, (0.1-1)atom layer(10^{-2}at%)	($10^{-4}-10^{-2}$) atom layer	1atom layer	1-1000ppm, (0.1-1)atom layer
30%	(1-10)%	(5-20)%	10%	(5-30)%
necessary	pure element correction	not		not
not	not	necessary	necessary	necessary
to do depth analysis by combining splashing techniques				

molecule are cut off and a small part in the form of positive and negative ion is splashed out. To analysize these secondary ion in a quality tester, there are two different methods: one is to scan the ion after focusing (diameter can be 1-300 micron) on the sample, and the other is not using scanning but the image formation method. The speed of splashing is very slow (0.1-10^{3}Å/ sec.) and it can be analysized layer after layer. One of the

characteristics is that it can have an overall analysis because the quality tester has high sensitivity.

Auger electron spectrum technique is to use electon bombardment sample of 3-5 KeV to make spectrum analysis of the Auger electronenergy produced by the bombardment. The diameter of electron beam is 25-100 micron (can be 10 micron),and the depth is 5-20Å. Thus it can be used to make surface impurity analysis. This technique has been comprehensively used. If it is combined with ion (1 KeV Ar^+ or Xe^+) source bambardment, it can have an Auger electron spectrum of the longitudinal impurity distribution.

Ion back scattering technique is to use ion (such as proton, $4He^+$) of KeV or MeV energy bumping with the elasticity of the surface atoms (blocking effect) to produce characteristic energy spectrum which indicates the mass of the scattering center.Thus the components of the external atoms can be known. Combining with splashing technique, it can learn the conditions of the longitudinal impurity. This technique is not suitable to light element but it can be used to study impurity and defect position of ion implantation layer. In addition, the X ray produced by Ar^+ ion bambardment can also be used to analysize surface components.

For perfection analysis of thin layer or surface structure, there have been such instruments as scanning electronic microscope, low and high energy electron diffraction and high pressure electronic microscope. All these instruments can be used together. The scanning electronic microscope can be used to make a scanning observation of the material surface, and its general recognition ability is $\sim$100Å, depth recognition rate can reach 200 Å, and its amplifying multiple is 20X - 2 10^8X. The high pressure electronic microscope

(1-3million volt) can penetrate 3-7 times deeper than an ordinary electronic microscope, so it can be used directly to obsreve samples of only several micron. As what is observed is close to the nature of semiconductor materials, it can have the relationship between macroscopic property and microscopic structure. A low energy electron diffraction of 5-500 eV can be used to analysize the atomic structure of several layers of the surface.

According to the principle of X ray extraorodinary penetration, and using the so-called appearance photograph technique, the defects of a piece of semiconductor material can be disclosed. This method has been widely used now, but it is not good for conditions of high defect density $>10^{6}\,cm^{-2}$, and its exposure time is very long (~ 10 hours). If there is a synchrotron accelerator X ray radiation, the magnitude of strength can be promoted to 3-6. It takes only a few second to take an appearace picture. The precision test of crystal lattice constant is also a very useful technique. The crystal lattice constant that so far can be tested by X ray interference technique is 10^{-8}.

2. Because of the development of thin film material techniques, the test of thickness of thin layer is a very important work. So far there have been more than 20 different methods. The thickness of thin layer is related to physical characteristics of the material. If the thickness is <100Å, the thin film can be considered discontinuous (island or hole); if the thickness is >100Å but <3000Å, the electric parameters,such as electric conductivity and Hall coefficiency, will be related to the thickness; and if it is >3000Å, the physical parameters will be close to the nature of semiconductor material. So the test of physical characteristics is often

carried out by a scale $> 3000\AA$.

The method used most widely to test thickness is the infrared reflection method. This method is nondestructive and it can be used to test Si film of more than 2 micron. But it can only test single layer and it requires that the resistivity of substrate (such as 10^{-2} ohm.cm) and epitaxial layer (>1 ohm.cm) must be different. Two reflection planes are parallel and the thickness fluctuation is <1 micron. For multi-layer structure, it uses first angle lap stain and then interference stripe to determine the thickness, the testing range is about 1 micron. There are round plate rolling method and cylinderial rolling method. The rolling is used first and then the standard staining method, and the testing range is ~ 1 micron. Elliptic measurement method (infrared, visible light) is nondestructive, and it can be used to test the thickness of insulating layer, and the testing range is about $10\AA$. Generally speaking, thickness test must combine with real situation. For instance, it is better to use ion isoabsorption peak value to test the thickness of thin film of $n = 10^{18}(cm)^{-3}$ GaAs, and the testing range is about 10^{-1} micron. In short, to test thickness <1 micron is still quite difficult.

3. For testing the electric characteristics of semiconductor thin layer, such as resistivity, carrier concentration and longitudinal distribution, and transferability, many useful techniques have been developed in recent years. Some of them ar shown in Table 11.

Using probe to test resistivity, the interstice between probes is generally larger than 600 micron. This technique can be used to heterogeneous epitaxial layer and isotype layer of which the epi-layer resistivity is much lower

than that of substrate. The resistivity expanding method can be used to both isotype and heterogeneous epitaxial layers, and after angle lapping, it can be used to test longitudinal distribution. But this kind of method always uses probe pressure and sometimes the thin layer is broken by the probe.

Table 11 Some of Epitaxial Layer Resistivity Testing Techniques

Testing method	resistivity range (carrier cm^{-3})	types of conduction	accuracy
Schottky potential barrier, C-V	$10^{13} - 10^{16}$	N/N	± 10%
Diffusion junction, C-V	$10^{13} - 10^{18}$	N/N or P/P	± 10%
Epitaxial junction, C-V	$10^{13} - 10^{17}$	N/N or P/P	± 10%
Four point probe	$10^{12} - 10^{20}$	N/P or P/N	± 2%
Spreading resistant probe	$10^{14} - 10^{20}$	all	± 10%
MOS electric capacity	$10^{12} - 10^{16}$	all	± 50%

The various (C-V) methods use (electric capacity ~ voltage) relationship as foundation to examine carrier concentration and longitudinal distribution. For GaAs, the secondary harmonic method has been used to register carrier longitudinal distribution. But, because the exhaustion layer is limited only the vicinity of (p-n) junction, this method is only suitable when carrier concentration is $< 10^{17} cm^{-3}$, and it cannot be used for poly-layer epitaxy.

Testing transferability of thin layer usually first uses supplementing sheet to the high resistant substrate and then the general testing method. But for testing a very thin layer which is < 1 micron, the problem is rather

complicated. Due to the surface scattering caused by the surface electric charge layer, the transferability is low. Of thin layer electric conduction structure and various surface effects, the theory has not yet become clear, so the problem of testing method has not been solved.

4. The fluorescence (photoexcitation or electron excitation) technique is the method which is mature and widely used in recent years. Through fluorescence peak analysis, the data concerning impurity, defect energy level, surface homegeneity, single impurity (defect) center or compound center. This method is nondestructive, simple and can be used to thin layer materials. It is now mainly used in the compound semiconductor of illuminant articles, such as GaAs, GaP. Further analysis, such as nonradiation compound action, has not yet started.

Using far infrared excitation spectrum (PTIS) under low temperature to study different kinds of impurity and their concentration in semiconductor materials has developed very well in recent years. The instrument used in this study is infaraed Michelson interferometer. It first finds out the interference spectrum of light strength and the movement of reflecting mirrow ΔX. Then through Fourier conversion, it has a Fourier conversion spectrum which is formed according to the frequency distribution. The energy range is usually within (0-15 MeV). Because this method is to excite the neutral donor (or acceptor) to a state of excitation, then using the phonon in the crystal to excite the electron (or vacancy) on the excited donor (or acceptor) onto the conduction band (or valence band) and finally using photoconductor to have the signal, the spectral line is therefore narrow, the signal noise is loud ($\succ 30$) and the recognition rate and the

sensitivity are high. Under favorable conditions, the concentration of low energy level impurity can be analysized to $10^7 cm^{-3}$.

To study impurity distribution in crystal lattice is an important and significant work. From the infrared absorption spectrum analysis of a local phonon, the impurity distribution in GaAs can be learned, such as silcon in gallium [Siga ($384cm^{-1}$)] (Si_{Ga}) or in arsenic [Sias ($399cm^{-1}$)] (Si_{As}). From strength analysis, the content of impurity can also be estimated. But this method can only be applied to heavy blending ($\geqslant 10^{18}cm^{-3}$) and to impurity of small mass and can form a local phonon, such as Li, B in Si and Si, C, Al, P, Li of GaAs. Another method is using the channel effect between ion (such as $4He^+$) of ~1 MeV and solid action to analysize the distribution of impurity atoms in crystal lattice. This method is only suitable for the heavy elements (such as As, Sb in Si) of high content ($\geqslant 10^{18}cm^{-3}$) or the fluctuating atoms of Si of $\sim 10^{20} cm^{-3}$. It is easy to analysize the atoms of substituional impurity, but the atoms of nonsubstitutional impurity is quite complicated. So this method is mainly applied to the diffusing and ion implantation layers. After the bombardment by the particle of ~ MeV, the sample itself is possibly damaged by the radiation.

5. The analysis of characteristics of semiconductor materials is a natural development of some deeper studies. From such studies, it can find out how to use these materials and how to improve the mass of the materials. So the semiconductor material physics has become an important and broad field of study. The following is some of the directions, which some of current studies have concentrated on.

The study of energy band structure is a fundamental subject in semiconductor physics. The development as well as the application achieved in this study is remarkable. In addition to the elements of Group IV, the compounds of Group 111-V and Group 11-V1 and the solid solutions among them have all been studied. The study of Te energy band structure which is much more complicated has also made considerable achievement. In laboratory techniques, it has developed the technique of how to modulate spectrum, and energy range has become much higher, such as ultraviolet electron spectrum (UPS).

The study of material transporting process concentrates on problems of strong electric field, hot electron movement and negative resistance of body effect. There are also many projects of studying sound-electric effect.

In recent years, the study of electron-vacancy combined illumination in theory as well as in application has made marvelous advancement, such as GaP, which has indirect band, can emit light through exciton that is bound by impurity. The work on heterogeneous jnuction has increased greatly and achieved some applications already. Accompanying the development of laser techniques, the study of semiconductor materials has entered into a new area, such as laser source Raman scattering.

Because the semiconductor articles have more and more concentrated on the vicinity region of the surface, and, in fact, there have been many surface effect articles, the study of surface has once again received great attention recently, such as the relationship of Si surface condition with

its inner condition; surface deposit matel of Si, GaAs and GaP; semiconductor film; the semiconductor surface potential barrier region; the boundary plane of Si-SiO_2; and SiO_2 layer.

6 Conclusion

Those as have mentioned above are the broad and important areas in the study of semiconductor materials and also concentrated points in the recent studies. The work on semiconductor materilas in China has come out of nothing, and in the 1950's, we achieved great advancement. In the 1960's, we achieved further development. From our experience, we have confidence that in the very near future,we can catch up with advanced level in the world.

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